EVALUATION OF TiB_2-G COMPONENTS

DOE Contract No. DE-FC07-90ID 13038

Final Report

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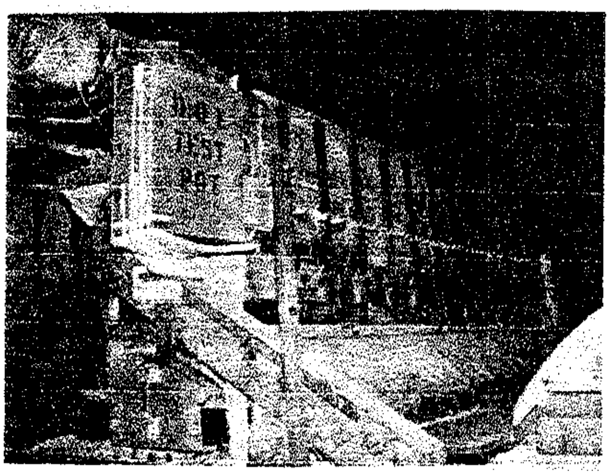
SUMMARY

Two 70 kA prebake aluminum reduction cells at the Kaiser Mead Smelter were retrofitted and operated with "mushroom"-shaped TiB_2-G cathode elements for 4 to 5 months to evaluate the technical and economical benefits, and test the durability of the newly developed TiB_2-G cathode material in an industrial environment as part of a joint cost-shared research program with the U.S. Department of Energy (DOE).

The tests demonstrated that when operating with mostly intact (near the design target coverage) TiB_2-G elements, the TiB_2-G cell operated at $\approx$ 8 % lower energy consumption than conventional cells due to a reduced anode-to-cathode distance. It also demonstrated that the cell insulation could be modified to allow operation at this reduced energy input.

The major problem revealed in the two tests was breakage of the TiB_2-G cathode elements. This problem prevented the energy consumption targets from being fully achieved and was a major contributor to cathode lining erosion. The breakage of elements was predominantly in the stem-to-top transition zone, where fabrication flaws in sectioned elements were evident. Additionally, contact between anodes and TiB_2-G elements, particularly following the metal tap operations, put mechanical stresses on the elements and possibly led to element breakage in the first test. Computer control parameters and operational procedures were developed and implemented which greatly reduced this possibility during the second test.

The excessive breakage of the elements prevents determining meaningful results as to the lifetime of the elements as well as determining fabrication costs. Thus, evaluation of the economics of the use of TiB_2-G cathode elements cannot be done.



DOE Test Cell at Kaiser's Mead Plant

TiB_2-G Element
Being Installed For Startup

INTRODUCTION

Reynolds Metals Company participated in a U.S. Department of Energy (DOE) sponsored and cost-shared research project "Evaluation of TiB_2-G Cathode Components Engineering Packages," as Cooperative Agreement DE-FC07-90ID13038 under the U.S. Department of Energy's Metals Initiative Act. The objective of the project was to develop and confirm the engineering packages needed as precursors to the industrial application of TiB_2-G wettable cathodes in alumina reduction cells as a retrofit modification.

Great Lakes Research (Sigri Great Lakes Carbon) was contracted to fabricate approximately 300 TiB_2-G cathode elements for two reduction cells and destructive testing, develop a quality assurance program, qualify suppliers of TiB_2 powders and conduct an economic analysis. Development of these elements and pilot scale testing had been conducted and documented by Great Lakes under the program "Long Term Testing and Evaluation of Cathode Components in a Commercial Aluminum Cell" under DOE contract DE-AC07-87ID12689.

Four primary objectives were identified for this new program in its Statement of Work in the proposal:

- Improve the cell insulation to allow operation at reduced energy levels,
- Modify the operating controls and procedures to prevent damage to the cathode elements during routine operation,
- Confirm acceptable lifetime of cathode elements in the form and engineering packages to be evaluated, and
- Demonstrate that the total decreased cost of aluminum production using this wettable cathode technology more than offsets the additional costs of the cathodes, enhanced controls, and extra precautions proven mandatory.

In accomplishing these objectives, eight separate tasks were identified as part of the program. These tasks were:

1. Fabricate TiB_2-G Cathode Components

   This task was primarily the responsibility of Sigri Great Lakes Carbon. Under this task were four subtasks.

   - Qualify alternate suppliers of titanium di-boride powder.
   - Develop a Quality Assurance Program for the manufacture of the elements.
   - Design and fabricate the cathode components
   - Perform an economic analysis considering reduced aluminum production costs and increased costs due to use of the cathode elements.

2. Develop and Fabricate Process Control Hardware and Software
   A specially designed control system was required to minimize the risk of damaging the cathode elements during operation.

3. Design Cells
   This task involved an improved insulation design, as well as other aspects of cell design to accommodate the cathode elements.

4. Construction of Cells
   This task was the actual cell constructions. Two cells were constructed for this testing.

5. Operation of Cells

6. Replace Cathode Components
   This task was planned to be a scheduled replacement of cathode elements (every three months) to further define their expected lifetime.

7. Document Cell Operations
   This task involved routine data collection and analysis of cell operation as well as intensive short term evaluation of cell performance by anode gas analysis and thermal evaluations.

8. Post Operation Analysis
   This task was directed toward cell and component autopsies to help determine life times and failure mechanism.

This report will serve as a documentation of the results of this test program.

BACKGROUND

Technology for a stable wettable titanium diboride (TiB_2) cathode is recognized as one of the most promising medium-term modifications to the Hall-Héroult process with the potential to substantially reduce the energy consumption required for the production of aluminum. The energy efficiency of conventional cells is only about 50%. The most outstanding feature of TiB_2 is its excellent wettability by molten aluminum which allows a thin aluminum film to be deposited on the TiB_2 surface without the presence of an aluminum pool. Hence, the anode-cathode distance can be decreased from about 2 inches to about 1 inch, corresponding to about a 1 volt decrease in cell voltage. This is impossible to accomplish in conventional cells due to the impact of magnetic forces on the large unstable aluminum cathode pool causing oscillating metal waves, uneven surface topology, and circulation patterns with high velocity components.

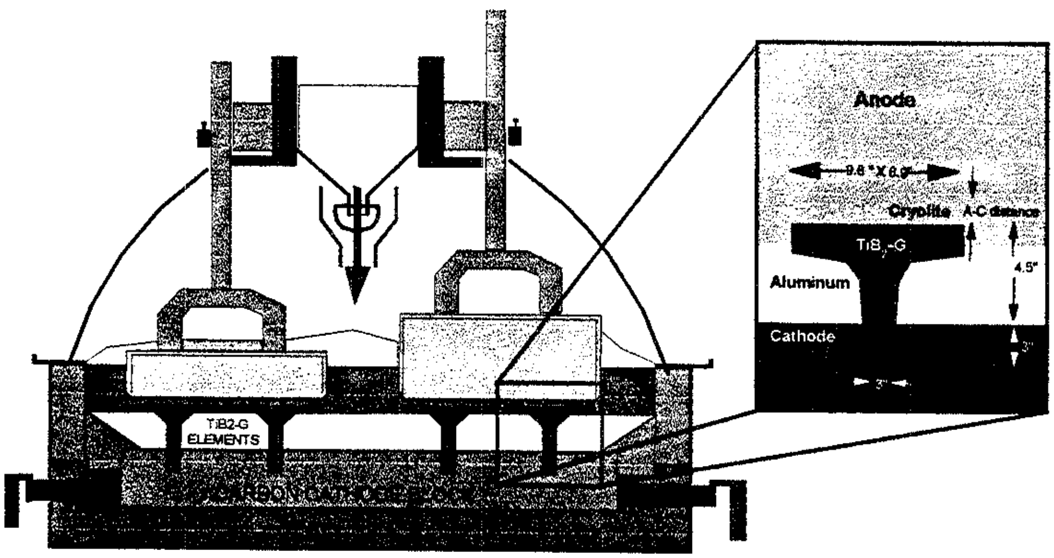


Figure 1. Prebake Cell Retrofitted With
TiB_2-G Elements in the Cathode

TiB_2 and various TiB_2-based composites have been investigated as wettable cathode materials for several decades, but these types of cathodes have not been commercialized (1). A major problem has been the long-term inability of TiB_2-based materials to survive the hostile environment. Significant progress has been made in recent years using TiB_2-carbon matrix materials that do not require expensive high purity powders and that have improved thermal shock characteristics.

- During 1985-1986 Great Lakes Research (GLR) and Reynolds Metals Company cooperated in a cost shared program with Electric Power Research Institute in the evaluation and development of solid TiB_2 shapes to be used in retrofitting aluminum reduction cells. This program resulted in manufacturing a favorable material, TiB_2-

graphite. The TiB_2-G material had shown promise in commercial cells as a stable, wettable cathode material demonstrating low dissolution rate and acceptable thermal shock resistance (2). Additional evaluation of the GLR TiB_2-G material continued in a cost shared program with GLR, RMC and the Department of Energy during 1987-1989.

- After additional material evaluation and modeling of thermal stresses in various TiB_2-G shapes, two "mushroom" shapes were evaluated in RMC's pilot reduction cell (3).

The earlier work demonstrated the suitability of the graphite containing TiB_2 material (TiB_2-G) for applications in reduction cells.

- Thermal shock resistance; this property was demonstrated to be excellent and is a key advantage for easy installation and removal during cell operation.
- Favorable geometry and size; large sizes and complex shapes can be fabricated.
- Durability; the TiB_2-G composite materials are not subject to breakage by slow crack growth mechanisms in the cell environment.

Additionally, TiB_2-G provides economic advantages by reducing the use of expensive TiB_2 since the TiB_2-G material has about 30 to 40% less TiB_2 on a weight basis relative to dense high-purity TiB_2 on an equal volume. TiB_2-G shapes are also estimated to be less expensive to fabricate by the GLR processes.

RESULTS

Program Time Line

This program was initiated in September of 1990 with completion in 1997. Several delays occurred during this time frame, resulting in the longer-than-planned period for the testing. The key events occurring during this program are summarized below.

• Contract Initiated	September /1990
• Design for a Troutdale Line 5 cell completed	June/1991
• Cathode element production initiated by Great Lakes Research – Initial 12 elements produced	June/1991
• Structural design of system software for process control completed	June/1991
• Testing of prototype anode current stem sensor and single anode with TiB_2-G elements conducted at Troutdale	August/1991
• Reynolds announces temporary closure of smelter capacity at Troutdale requiring relocation of test program	September/1991
• Sub-contract awarded to Kaiser Aluminum & Chemical Corporation to perform testing at their Mead facility	September/1992
• First cell startup at KACC	February 3, 1993
• Excessive breakage of elements leads to redirection of work to determine failure causes	April/1993
• Failure of first cell	June 28, 1993
• Relocation of Great Lakes Carbon fabrication facility for TiB_2-G elements from Elizabethton, Tn to Niagara Falls, NY	December/93 – August/94
• Completion of fabrication of elements for the second cell	October/95
• Second cell start-up	February 21, 1996
• Cell characterization study	April, 1996
• Termination of second cell testing	May 31, 1996

As depicted in the above time line significant delays in the test program occurred with the temporary shutdown of Reynolds' Troutdale location and the relocation of Great Lakes Research facility to Niagara Falls. In addition, the unexpected failures of the TiB_2-G cathode elements resulted in a redirection of work efforts as well as failure to complete some of the planned objectives.

Cell Design

The project plan was to operate two cells with the TiB_2-G cathode elements. The first cell test was originally scheduled for startup in November 1991, at Reynolds Metals' plant in Troutdale, Oregon, but was relocated to Kaiser's Mead Works, Washington, due to the temporary shutdown of the Reynolds' Troutdale smelter. Both plants have similar cell technology.

Initial cell design was completed for the Troutdale plant. Key parameters of this design include:

- Increased sidewall and cathode bottom insulation to achieve the desired energy conservation.
- A cathode tapping well to assure that the aluminum metal pad can be maintained below the top of the TiB_2-G elements.
- Point feeders to allow close and incremental control of alumina fed to the cell.
- An anode current sensor system facilitating continuous monitoring of anode current. This allowed detection of anodes operating too close to the TiB_2-G elements, prevented physical damage from occurring to the shapes and provided a record of the current distribution.
- Design of the TiB_2-G elements and the method for holding them in the carbon anode. A carbon cathode block was located under each anode, with appropriate holes machined in them to hold the stem of the TiB_2-G elements. Utlization of a narrower than standard cathode block was required to accomplish this, requiring modifications to the cathode shell and cathode strap connections to the bus.

Details of this design are presented in Appendix I.

Minor difference existed between the cells at Troutdale and Kaiser's Mead Works, requiring small adjustments in cell design. The thermal design was revised based upon discussions with Kaiser personnel. The final design is presented in Appendix II. The cell was designed to operate at 3.79 volt, 0.626 volt lower than standard cells. This was based upon a cell operating with 65% anode coverage by the TiB_2-G cathode elements and a 2 cm anode to TiB_2-G distance.

The insulation package for the first cell design included:

- Vermiculite insulation in the end walls and side walls protected by a steel vapor barrier
- Vermiculite and calcium silicate in the bottom protected by dry-barrier powder, castable refractory and a steel plate.

With the excessive element failures during operation of the first cell, which did not allow operation at targeted conditions, the second cell's thermal design was modified for a more conservative energy savings. Target operating voltage was 4.2 volts. The major change from the previous design was a reduced sidewall insulation utilizing low porosity firebrick and silicon carbide slabs. Details of this design are presented in the report "Thermal Analysis of the DOE TiB_2-G Retrofitted Aluminum Reduction Cell," attached in Appendix III.

The end view of an industrial prebake cell retrofitted with TiB_2-G cathode elements is shown in Figure 1. The "mushroom" shaped TiB_2-G elements produced for the first cell had a rectangular 24.1 cm x 16.5 cm x 2.5 cm (9.5 in. x 6.5 in. x 1 in.) thick top plate that transitions to a 7.6 cm (3 in.) diameter stem. Cathode elements produced for the first cell weighed approximately ≈ 15.5 lb. (7.0 kg). Four of these elements were located under each of the 24 anodes in the Kaiser cell, resulting in a coverage ratio of 64% (total TiB_2-G top plate area to total anode bottom area).

Modifications were made to the elements produced for the second cell and will be discussed later.

Computer Control System

The computer control system used was similar to Reynolds' standard control system with specific options added to protect the TiB_2-G elements. Figure 2 shows the pot control panel along with the display screen for the anode stem current monitoring system. Key modifications of the control system include the following.

- Individual anode stem current monitoring was developed for this system. A field mounted panel, as well as one in the office, displayed the individual current to each of the 24 anodes on the cell. The current was determined by measuring the voltage drop across a 4.5 inch distance on the anode stem. Anode stem readings were made about once a second during a two-minute period, with the readings normalized to the base line current. At the end of two-minute period, the computer would calculate and display
    - Average millivolt drop value for each anode
    - Standard deviation of the readings during each two-minute period
    - High and low millivolt value for all 24 anodes

  When a predetermined threshold limit was exceeded, an alarm message on the computer host system was annunciated. Anode stem reports were also generated by the system.
- Temporary voltage was applied to the setpoint at tap and then ramped off during the next 24 hours. As current was being conducted both through the elements and metal pad, when the cell was tapped a voltage increase was seen as less current was being conducted to the metal pad. This system was directed toward maintaining a constant anode to TiB_2-G distance.
- The system also detected non-linear down moves, indicating possible shorting to the TiB_2-G elements. When this was detected, temporary voltage was added to the system to prevent damaging the elements. Modifications were also made to the standard program to minimize the size of the actual down moves.

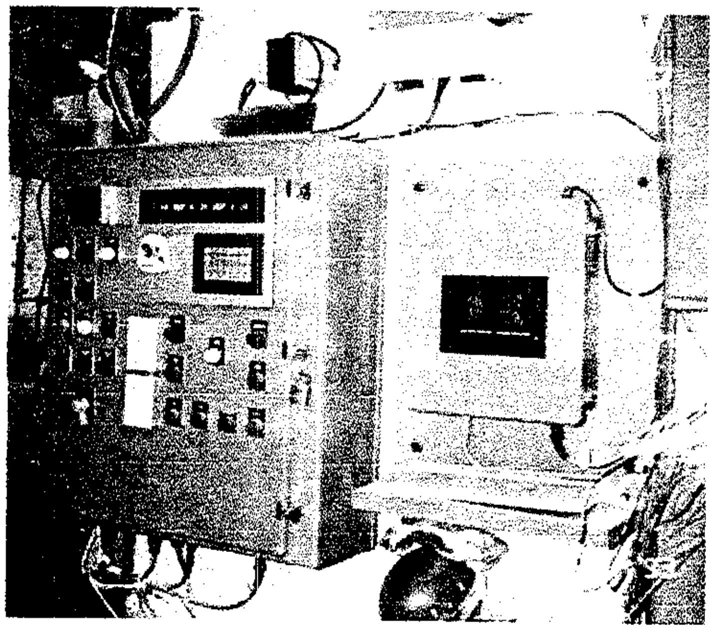


Figure 2. Pot Control Panel with Stem Sensor Display to Right

Cell Start-up

First Cell Start-up

All 96 TiB_2-G cathode elements were installed into holes machined into the cathode blocks of Cell 68 in Line 1 at the Kaiser Mead Works prior to the cell preheat and start-up. The cell was preheated for 24 hours using a gas bake manifold with multiple burners. The anodes were raised 1-2 inches above the top plate surface of the TiB_2-G elements.

Cell 68 was started on February 3, 1993, by first pouring molten aluminum and then molten cryolite into the tap end of the cell and bringing the molten bath into contact with the anodes. The cell was initially operated at 8 to 9 volts for a period of time to ensure proper bath temperatures. The cell voltage was then gradually reduced to a 4.0 voltage set point and the cell was operated at that point for two weeks.

Second Cell Start-up

The second cell start-up procedure was modified to give a more gradual heat up of the elements. The cell was gas baked over a two day period, melting 2000 lbs of aluminum pigs placed in the cell. Figure 3 shows the cell being prepared for start up with the aluminum pigs placed in the cell, the elements in place, and several anodes installed. Additional aluminum shot was added to the cell periodically during the gas bake to bring the molten metal pool above the top of the cathode elements. After achieving acceptable cathode and metal temperatures, bath was poured into the cell and electrolysis was started.

After start-up the voltage setpoint on the second TiB_2-G cell was intentionally controlled at 4.2 volts (0.2 volts higher than the first cell) to reduce the risk of contact between anodes and elements during the early periods of operations. The cell was operated at this setpoint without any operational difficulty.

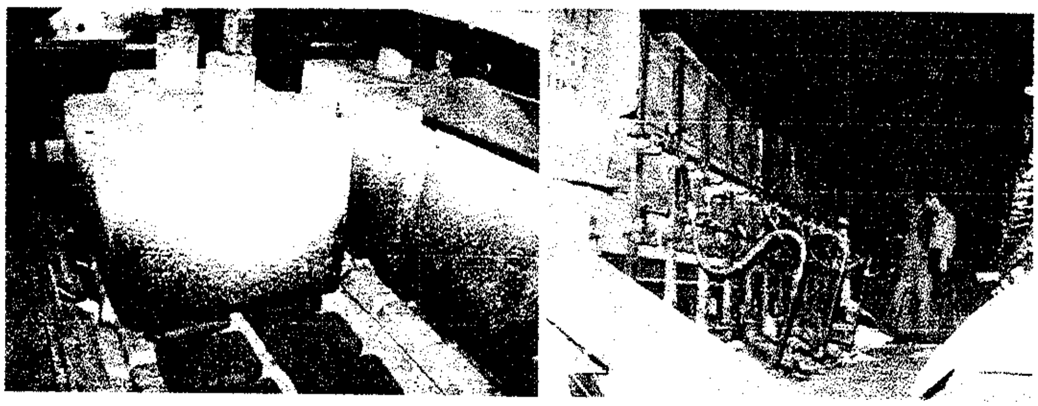


Figure 3. Startup of Cell - (Left) Location of Elements Under Anode and Aluminum Pigs - (Right) Gas Baking Manifold

Operational Procedures

In operating the cell a number of modifications to standard prebake cell procedures were required. These are summarized below.

<u>Anode Change</u>

Anode change is the most critical operation performed on the TiB_2-G cathode cell due to the potential for damage to the cathode components. Care has to be taken to ensure that the jackhammer and bars used to break the crust do not damage the cathode components, and that the anode is not dropped down into the bath onto the TiB_2-G elements.

Two anodes were changed every day on the day shift to give a 12-day anode cycle. Anodes were preheated using a gas burner in a metal box several hours before the change operation. Anodes were changed in a continuous sequential pattern around the cell. Each one was removed and set individually. Anodes were set in the cell at a height "referenced" to the height of anodes removed from the cell. Alternatively, anodes were also set at a fixed distance above the TiB_2-G elements, since the top of the elements are at a stationary location in the cathode cavity.

The four TiB_2-G elements under the two anodes were inspected using a metal rod as each anode was removed from the cell. The condition of the top surface of each TiB_2-G element was recorded and in some instances if severely broken (e.g., if more than half of the entire top plate was missing) the element was replaced using a "hot exchange" technique. The process control system automatically added temporary voltage at the anode change operation and was ramped-off at a predetermined rate.

Figure 4. Hot Exchange of TiB_2-G Element

Anode Bridge Raise Control

The moveable anode bridge on the Kaiser Mead cell is normally raised every 4 days. It was necessary to raise the anode bridge on the TiB_2-G cell daily due to the location of the anode current stem clamps between the moveable anode bridge and the lower anode hooding support on the anode superstructure.

Metal Tap

Metal tap of the TiB_2-G cathode cell is different from that experienced in standard cells. During metal tap of a standard cell, as the metal is removed and the metal level in the cell is reduced, the anode is lowered an amount equal to the decrease in metal level to maintain a constant anode-cathode distance and cell voltage. In a cell with TiB_2-G elements the anode-to-TiB_2-G distance remains constant as the metal level is reduced. Therefore, there should be little change in the cell voltage during tap without any movement of the anodes. The amount of voltage change expected is directly related to the amount of anode coverage by the TiB_2-G elements. The major concern during tapping is not to allow the anodes to move down (as done in conventional cells) and contact the TiB_2-G cathode elements.

When most TiB_2-G elements were intact, the voltage increase after metal tap was small, 50 to 100 mV, and when a significant number of the elements were broken (reduction in anode coverage area from 62% to 45%), the voltage increase after tap was large, 300 to

600 mV. The voltage increase depends on the extent of breakage and also the metal level in the cell due to increased current flow to the metal pad. The process control system added temporary voltage after tap and ramped-off the temporary voltage by lowering the anodes at intervals over a period of time. When anodes made contact with elements, it was indicated by the individual anode monitoring system. Contacts occurred more often when operating with a large number of broken elements, particularly following the metal tap operation while the temporary voltage was being ramped-off.

Anode Effects

It was extremely difficult to extinguish anode effects in the TiB_2-G cell as they could not be "killed" in the conventional manner of lowering the anodes until the anodes shorted to the metal pad. Anode effects were "killed" by the cell operators in 4 to 5 minutes by inserting green wood poles carefully in the metal pad between the TiB_2-G elements. The anode effect frequency of the TiB_2-G cell was half of that experienced for the standard cells, 0.5 versus 1.0 anode effect per pot day.

Element Breakage

First Cell

It was evident that a large number of the TiB_2-G elements was broken during the startup period and the first 12 days of cell operation. Thereafter, the breakage was slower, but still continued.

- Of the original 96 elements at startup, 35 (37%) were found to be damaged during the first anode inspection cycle. Damaged elements had either one-quarter or half of the full top plate missing. In all cases the stems were not fractured.
- 20 severely broken elements were replaced with new elements.

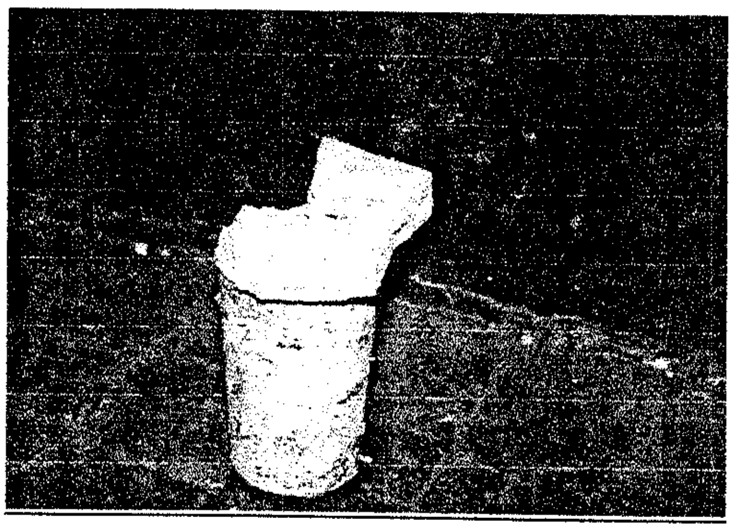


Figure 5. Typical Element Breakage

Table I. Breakage and Replacement of TiB_2-G Elements at the Anode Change Cycle

Anode Cycle	1st Inspection	2nd Inspection	3rd Inspection	Total
No. OK	61	53*	57*	
No. Damaged	35	43*	39*	
No. Replaced	20	4	8	32

*Includes original and replacement elements

Significantly more breakage occurred on anodes 13-24 (upstream side) than on the other side of the cell. The breakage rate was reduced for the second and third change cycle. In March the TiB_2-G cathode coverage of the anode decreased sharply to 42% due to the total breakage. The element breakage continued to occur in the TiB_2-G cell until the cell was stopped in June. No additional element replacements were made after March. A summary of the status of different grades of elements at the end of six inspections (April 16) is given in Table II. The breakage was higher for the replacement elements versus the original elements. There was no significant difference between the Grade A and B elements. The "Grades" were assigned to the elements at the time of manufacturing by Sigri Great Lakes Carbon, based upon their visual inspection. Grade A elements had no visible defects, while those classified as Grade B showed some surface defects.

Table II. Summary of Breakage of Original and Replacement TiB_2-G Elements in the First Cell

Classification of Elements	Orig.	Grade A Repl.	Grade B Repl.	Other
Total Installed	96	24	15	6
No. OK	26(27%)	8(33%)	3(20%)	6
No. > Half	19(20%)	7(29%)	3(30%)	2
No. < Half	10(10%)	5(21%)	7(47%)	2
Removed	41(43%)	4(17%)	2(13%)	2

Metal Impurities

The impurities measured in the aluminum of the first TiB_2-G cell demonstrate the expected increase in boron and titanium to their maximum solubility levels in aluminum.

- Boron increased from 1 ppm to 8-9 ppm
- Titanium increased from 66 ppm to 90-100 ppm

Table III. Monthly Metal Analysis of TiB_2-G Cell

	Line 1 ppm	Feb. ppm	Mar. ppm	April ppm	May ppm	June ppm
B	1	9	8	9	9	8
Ti	66	89	115	89	86	99

<u>Causes of Element Breakage in the First TiB_2-G Cell</u>

Breakage of TiB_2-G element was caused by a combination of flawed elements and exposure to mechanical stresses during cell start-up and operation.

Material, Fabrication, and Design Concerns

- Nearly all failures occurred across the top plate in the same manner as fabrication failures.
- Cross-sectioning of both elements that had been in the cell and elements that had not been in the cell revealed an extensive network of cracks inside their bulk.
- Large cracks were also evident in the transition area between the stem and the top plate of new elements.
- The internal microstructure of the elements was different from that of elements produced for the pilot cell test.
- Additionally, it was noted that several process changes by Sigri Great Lakes Carbon were made for the scale up in production, necessary for producing a large number of elements for the industrial cells.

Additional information on the structural analysis of these elements can be found in Appendix IV.

Impact of Cell Operations on Element Breakage

<u>Cell start-up:</u>

- Loss of TiB_2-G material occurred on the surface of the elements during the cathode gas preheat stage due to oxidation at the high temperatures.
- An anode stem burn-off (anode falling onto several elements) occurred immediately after start-up due to an unstable metal pad.
- The potential existed for mechanical damage of elements due to several large additions of molten bath and metal additions at the tap end of the cell and between anodes.

Cell operations:

- Over-tapping caused a squeezed anode-to-TiB_2-G distance or a higher temporary voltage operation, particularly with broken elements.
- Control of the anode lowering operation is critical to prevent making contact between anodes and elements when ramping-off temporary voltage after the metal tap operation.
- Operating for extended periods with low alumina caused the anode-to-TiB_2-G distance to become squeezed and increased the risk of potential contact between anodes and elements.
- The impact of anode effects on causing damage to the elements was unknown.
- The anode bridge was not completely level causing the anodes on the up-stream side of the cell to be higher than the anodes on the down-stream side.

Second Cell

Changes in Element Design, Fabrication and Operations for the Second TiB_2-G Cell

- The element "mushroom" shape was redesigned to reduce stresses in the "transition" area. A new forming mold was designed with improved material flow characteristics. The new design added some mass in the stem-to-top transition zone, and the top plate thickness.

- Adjustments in the molding parameters included a greatly reduced bake rate, a faster sintering rate, and an increase in the pitch content.

Inspection and Replacement of TiB_2-G Elements

Despite the redesign of elements, changes in the fabrication processes, and improvements in the cell operational procedures, significant breakage of elements occurred immediately and continued throughout the operation of the second TiB_2-G cell. There was still a significant crack network within the elements as experienced in those for the first cell.

- The breakage of elements and replacement on the first inspection cycle was significantly lower than experienced for the first cell, 15 versus 35 damaged elements.
- The breakage of elements continued on following inspections and was higher on the second and third inspection cycles than experienced for the first cell.

Table IV. Breakage and Replacement of TiB_2-G
Elements at the Anode Change Cycle

	1st Inspection Cycle 2/23-3/5	2nd Inspection Cycle 3/6-3/17	3rd Inspection Cycle 3/18-3/29
No. Broken	15	34	50
No. Replaced	6	10	1
Total No. Replaced	6	16	17

To ensure maximum element coverage for cell characterization and performance tests in May, all of the elements were inspected in April; 51 elements were replaced leaving only 10 of the 96 partially damaged elements in the cell. The TiB_2-G top plate coverage was 97% of the total (62% cathode-to-anode area ratio) at this point.

Table V. Summary of Breakage to Original and Replacement TiB_2-G Elements in the Second Cell

Classification of Elements	Orig. A	Orig. B	Repl. A	Repl. B
Total Installed	64	32	43	67
No. OK	6	4		
Damaged	60	28		
Avg. No. Days in Service	52*	38*	22	19

*Excluding unbroken elements

Metal Impurities

The impurities measured in the aluminum of the second TiB_2-G cell demonstrate an increase in boron and titanium to their maximum solubility levels in aluminum similar to that experienced in the first cell.

- boron increased from 1 ppm to 10-20 ppm
- titanium increased from 66 ppm to 90-100 ppm

Table VI. Monthly Metal Analysis of TiB_2-G Cell

	Feb. ppm	March ppm	April ppm	May ppm
Boron	11	10	10	20
Titanium	386	92	110	110

Cell Performance

First TiB_2-G Cell

The first TiB_2-G cell was operated at a 4.0 volt setpoint for the first two weeks without any operational difficulty, confirming that the technical goal of the project could be met. In February, the energy consumption for the TiB_2-G cell was 7 % less than the standard cells in Line 1. However, the difference decreased each month thereafter as shown in Table VII. Eventually, operations were adversely affected by the excessive breakage of the TiB_2-G elements. Consequently, the monthly energy and production results were less than the performance target. The increase in energy consumption each month is related to the increase in breakage of TiB_2-G elements as more current is being conducted directly to the metal pad. The continued decrease in aluminum production corresponded closely with the increased breakage of TiB_2-G elements.

Due to continued breakage of elements, the primary emphasis was shifted in April to fine tuning operational procedures and determining the cause of breakage. While cell performance data was still reported it was not considered representative of a cell fully equipped with TiB_2-G elements.

Table VII. Monthly Performance Data for the Operation of the First TiB_2-G Cell February 3 to June 28, 1993

	Line 1	TiB_2-G Cell				
Parameter	Average	February	March	April	May	June
Line Amperage, kA	68.595	68.910	68.750	68.290	68.510	68.590
Cell Voltage, V*	4.496	4.225	4.332	4.352	4.395	4.515
Aluminum, lb/PD	1130	1121	1084	1103	1100	1092
Current Efficiency, %	92.8	91.7	88.9	91.0	90.5	89.7
DCkWhr/lb Al	6.69	6.23	6.59	6.47	6.57	6.81
AE/PD	1.18	0.9	0.65	0.43	0.52	0.50
Cathode Drop, mV		0.221	0.219	0.223	0.020	
Instability, mV			0.025	0.020	0.224	0.030
Temperature, °C	963	966	968	968	969	967
Bath Ratio	1.06	1.09	1.09	1.05	1.06	1.05
Metal Before Tap, in.		3.6	3.41	3.41	3.08	3.26
Metal After Tap, in.			2.49	2.42	2.12	2.36

* Excluding 100 mV bus drop between cells

Second TiB_2-G Cell

The operations of the second test cell (Cell 68) were also adversely affected by the excessive breakage of the TiB_2-G elements and as a result the performance data did not achieve the target. The continued decrease in aluminum production each month corresponded to the increased breakage of TiB_2-G elements.

After reviewing the element breakage following the first complete change-out of anodes, the setpoint was increased to 4.40-4.60 volts.

With the replacement of 31 elements in April, the setpoint was again decreased to 4.2 volts in preparation for cell performance tests in May.

Table VIII. Monthly Performance Data for the Operation of the Second TiB_2-G Cell February 21 to June 1, 1996

	Line 1	TiB_2-G Cell				
	Average	February	March	April	May	YTD
Voltage*	4.606	4.651	4.688	4.560	4.46	4.58
Amperage, kA	68.830	68.830	69.300	69.840	69.970	69.650
Aluminum, lb/PD	1126	1316	1126	1103	1067	1119
Current Efficiency, %	91.2	107.6**	91.4	89.0	86.0	90.5
DCKWH/lb Al	7.03	6.04	6.87	6.93	7.25	7.02
AE/PD	1.23	0.89	0.11	0.57	0.52	0.46
Instability, mV		0.045				
Cathode Drop, mV						
Bath Temperature, °C	960	962	963	962	964	963
Ratio	1.10	1.16	1.15	1.17	1.16	1.16
Metal, B.T.		5.0	4.6	3.9	4.1	4.3
Metal, A.T.		3.25	3.2	3.0	3.1	3.1

* Excluding 100 mV bus drop between cells
**New cell

Performance Characterization

Current Efficiency Analysis

The operational performance of the 70 kA prebake cell retrofitted with TiB_2-G cathode elements was compared with a conventional prebake cell in a comprehensive process characterization study at the Kaiser Mead Smelter.

As shown in Table IX, the tests confirmed that the TiB_2-G cell can operate at approximately 9% lower energy consumption than conventional cells due to a reduced anode-cathode distance when operating with mostly intact TiB_2-G elements while maintaining constant current efficiency. Full details of the current efficiency study are presented in Appendix V.

Table IX. TiB_2-G Cell Performance

	Conventional Prebake Cell	Retrofitted TiB_2-G Cell
Decomposition Voltage, V	1.212	1.212
Anode Overvoltage, V	0.558	0.565
Cathode Overvoltage, V	0.089	0.089
Bath Drop, V	1.99	1.64
Anode Drop, V	0.512	0.474
Cathode Drop, V	0.310	0.290
Pot Meter Volts	4.671	4.270
A-C Distance, inch	1.60	0.78
Production, lb Al/PD	1167	1160
Current Efficiency, %	93.7	93.2
Line Amperage, kA	70.14	70.14
DC kWh/lb Al	6.740	6.194

Thermal Analysis

In addition to the current efficiency analysis conducted on the test cell, a partial thermal study was conducted. Surface shell temperature measurements were obtained for four "slices" of the cathode, where a "slice" is defined as the area between and including two cradles. The measured heat losses for the TiB_2-G retrofitted cell compared well to the two-dimensional finite element modeling conducted on the cell design. Details of the thermal analysis are presented in Appendix III.

DISCUSSION

While excessive breakage of the elements in both cell prevented long term operation at reduced anode-to-TiB_2-G distance, the test program did confirm several important aspects of operation with TiB_2-G cathode elements.

- During a brief current efficiency study in which all elements were nearly intact, operational performance was measured at an anode-to-TiB_2-G distance of 0.8 inch. With this operation, cell voltage was reduced by 0.4 volts over standard operation with essentially no change in current efficiency. This reduction in voltage is not as great as may be expected if the TiB_2-G material provided more of the active cathode area. A significant amount of the current was still conducted directly to the metal pad. This was especially pronounced at metal tap, when voltage would increase by 0.3 to 0.5 volts. The amount of increase was related to the amount of element breakage, as well as to where the metal level was prior to tap.
- Element breakage was the reason for failure to achieve long term operation at reduced voltage. The dominant reason for breakage was related to the internal cracks within the elements. These cracks were formed during the processing of the materials primarily due to the rather complicated shape of the elements. While redesign of the element shapes, in particular the stem to plate transition area, did help reduce this problem, it could not be eliminated.
- Operational procedures developed during this program provided an adequate means of control for the cell. Modifications to the computer program to prevent direct contact with the elements worked well; however, due to the breakage of the elements, full evaluation of the system and procedures could not be done.
- The cathode insulation package developed for the cell proved sufficient for maintaining a thermal balance at reduced voltage. Failure of the first cell (tap out) occurred because the insulation package was designed for an operation at less than 4.0 volts, while element breakage dictated operation around 4.5 volts.

Based upon the test work, it is clear that TiB_2-G materials can be used in a reduction cell. However, future direction of the work will be to develop a method of using the material in a much simpler form, such that processing of the elements does not contribute to failure. While operation with elevated tiles provide a means of using the materials in a retrofitted cell design, other means such as using a drained configuration to a sump, should be explored. Future work should be directed toward eliminating internal flaws within the TiB_2-G elements such that breakage does not occur while implementing the operational and control procedures developed during this program.

REFERENCES

1. McMinn, C. J., "A Review of RHM Cathode Development," Light Metals, 1992, p. 419-425.
2. Tucker, K. W., Gee, J. T., Shaner, J. R., Joo', L.A., Tabereaux, A. T., Stewart, D. V., Richards, N. E., "Stable TiB_2-Graphite Cathodes for Aluminum Production," Light Metals, 1987, p. 345-349.
3. Alcorn, T. R., Stewart, D. V., Tabereaux, A. T., Joo', L. A., Tucker, K, W., "Pilot Reduction Cell Operation Using TiB_2-G Cathodes," Light Metals, 1990, p. 413-418.

APPENDIX I

CELL DESIGN FOR A TROUTDALE REDUCTION CELL WITH TiB_2-G CATHODES

REYNOLDS METALS COMPANY
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September 8,1998

Mr. John A. Yankeelov
U.S. Dept. of Energy
Idaho Operations Office
850 Energy Drive
M.S. 1225
Idaho Falls, ID 83401-1563

Dear Mr. Yankeelov:

Subject: **Transmittal of Draft Copy of Final Report for Evaluation of TiB_2-G Cathode Components, DE-FC07-90ID 13038**

Enclosed is the draft copy of the final report for the Evaluation of TiB2-G Cathode Components contract. Upon review of this document, please forward your comments to me as soon as possible, so that I may submit the final version of this report.

Sincerely,

Tom Alcorn

T. R. Alcorn

COPIES: Linda Hallum, Contract Specialist
Sara Dillich, Program Manager